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(54) Title: SHAPED OXIDATION CATALYST STRUCTURES FOR THE PRODUCTION OF MALEIC ANHYDRIDE

(57) Abstract

Shaped oxidation catalyst structures containing catalytic material comprised of mixed oxides of vanadium and phosphorus which are useful for the production of maleic anhydride via the partial oxidation of nonaromatic hydrocarbons, particularly n-butane, in the vapor phase with molecular oxygen or a molecular oxygen-containing gas are provided. Such structures are characterized by exhibiting (a) a geometric volume of from about 30 percent to about 90 percent of that exhibited by the void space-free solid geometric form, (b) an external geometric surface area/geometric volume ratio of at least about 15 cm^{-1}, (c) a bulk density of from about 0.4 g/cm^3 to about 1.4 g/cm^3, and (d) a mechanical resistance sufficient to maintain substantially the structural integrity of the shaped structure under handling and use conditions.
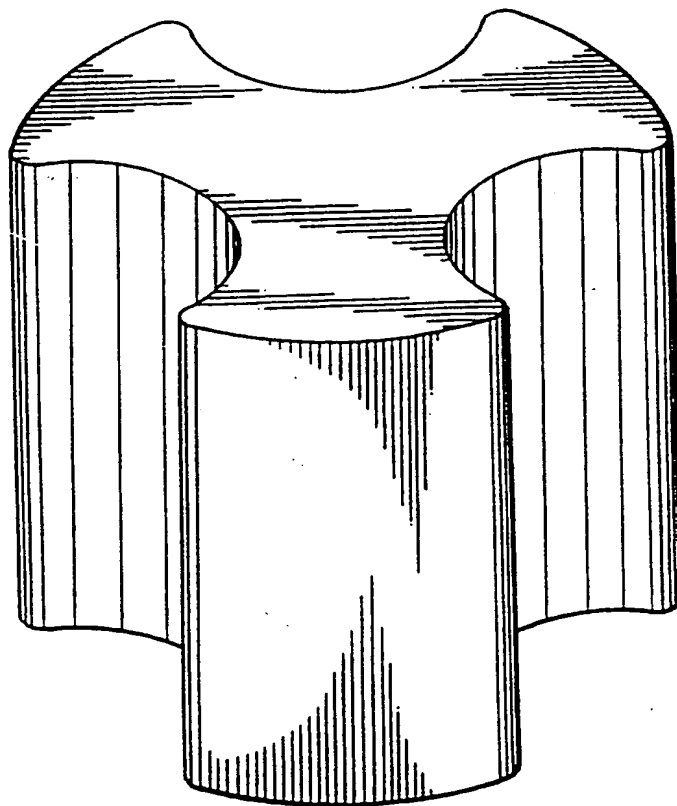
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SHAPED OXIDATION CATALYST STRUCTURES
FOR THE PRODUCTION OF MALEIC ANHYDRIDE
BACKGROUND OF THE INVENTION

5   1. Field of the Invention

This invention relates to shaped oxidation catalyst structures. More particularly, this invention relates to shaped oxidation catalyst structures containing catalytic material comprised of mixed oxides of vanadium and phosphorus which are suitable for the production of maleic anhydride via the partial oxidation of nonaromatic hydrocarbons in the vapor phase with molecular oxygen or a molecular oxygen-containing gas.

15   2. Description of the Prior Art

The physical form of a catalyst in heterogeneous catalysis is known to be an important factor governing the activity and productivity thereof. In general, a given catalyst exhibits increased activity as the particle size of the catalyst is decreased. However, in fixed-bed reactor systems, a decrease in catalyst particle size results in an increase in pressure drop across the catalyst bed. This phenomenon results from close packing of the catalyst particles in the catalyst bed. And as the pressure drop across the catalyst bed increases, the amount of reactant gas that can be passed through the catalyst bed at a fixed inlet pressure becomes limited. Conversely, as the catalyst particle size is increased to improve pressure drop across the catalyst bed, some loss of catalyst activity results from, _inter alia_, the effect of lower catalyst charge density, that is, quantity of catalyst per unit of reactor volume.

In an attempt to overcome the difficulties experienced with respect to catalyst activity and productivity and pressure drop across the catalyst bed, a number of catalyst shapes have been described in the prior art.

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U.S. Patent Nos. 4,370,492 and 4,370,261 describe
star or ribbed rod catalyst carrier shapes as being
useful for supporting active metals for the production
of vinyl acetate in the gaseous phase reaction of

5   ethylene with acetic acid and [molecular] oxygen or
[molecular] oxygen-containing gases.
U.S. Patent Nos. 4,342,603 and 4,328,130
describes a hydrocarbon conversion catalyst having
substantially the shape of a cylinder having a

10 plurality of longitudinal channels extending radially
from the circumference of the cylinder and defining
protrusions therebetween. The protrusions are
described as having maximum widths greater than the
maximum widths of the channels.

15 U.S. Patent Nos. 4,133,777 and 4,116,819 describe
catalysts in the shape of elongated extrudates having
alternating longitudinal grooves and protrusions on
the surface. Such catalysts reportedly are useful for
hydrodesulfurization of residual petroleum oils, coal

20 liquids, shale oils, and oils from tar sands.
U.S. Patent No. 3,966,644 describes shaped porous
catalysts that are defined as concave geometric
cylinders which are polylobal in shape. The catalysts
reportedly are useful in the hydrotreating of

25 hydrocarbons with increased catalyst efficiency over
conventionally shaped catalysts.
In U.S. Patent No. 3,957,627, a substantially
spherical catalyst having a void center and a hole
extending to the external surface is described as

30 being useful for hydrotreating a hydrocarbon feed
stock containing compounds with carbon-sulfur bonds,
carbon-nitrogen bonds, and/or carbon-oxygen bonds.
U.S. Patent No. 3,347,798 discloses hollow bead
catalysts which reportedly are suitable for use in a

35 wide variety of fluidized bed reactions, for example,
in the hydrogenation, oxidation, dehydrogenation,
dehydration, polymerization, condensation, amination,
reduction of aromatic nitro compounds, cracking,

refining and reforming of hydrocarbons, alkylation of
hydrocarbons or their derivatives, and also aromatic
amino, nitro and aminonitro compounds by reduction or
reaction with alcohols, and also the production of
5   alkanolamines, diamines, diphenylamine, and imines.

In spite of the foregoing, however, catalysis
remains basically an inexact science, that is, an
empirical art unenlightened by rules decreeing
certainty and predictability. Thus, the directional
10 effect of catalyst shape on a particular catalytic
reaction with a particular catalytic material is not
predictable. Primarily, this is due to each catalytic
reaction having unique reaction kinetics and the
catalyst utilized having unique forming
15 characteristics.

The production of maleic anhydride via the
partial oxidation of hydrocarbons in the vapor phase
with molecular oxygen or a molecular oxygen-containing
gas in the presence of a vanadium phosphorus oxide
20 catalyst is one such reaction. Maleic anhydride is of
significant commercial interest throughout the world.
It is used alone or in combination with other acids in
the manufacture of alkyd and polyester resins. It
also is a versatile intermediate for chemical
25 synthesis. Significant quantities of maleic anhydride
are produced each year to satisfy these varied needs.

Various oxidation catalysts and oxidation
catalyst shapes and techniques have been used in the
production of maleic anhydride, particularly the
30 partial oxidation of nonaromatic hydrocarbons having
at least four carbon atoms in a straight chain (or
cyclic structure). In general, such catalysts contain
mixed oxides of vanadium and phosphorus. More par-
ticularly, such catalysts wherein the valence of the
35 vanadium is between about +3.8 and +4.8 are considered
as being especially well-suited for the production of
maleic anhydride from saturated hydrocarbons having at
least four carbon atoms in a straight chain. In many

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instances, such catalysts also contain added promoter elements which are considered to exist in the catalysts as the oxide.

5   U.S. Patent No. 4,283,307 describes an oxidation catalyst structure for the production of maleic anhydride which comprises a cylinder having a bore therethrough and is further described as consisting essentially of catalytic material comprised of a phosphorus, vanadium, oxygen complex.

10   U.S. Patent Nos. 4,181,628 and 4,178,298 describe (solid) pellets (cylinders) as a suitable oxidation catalyst structure for the production of maleic anhydride.

       U.S. Patent No. 4,632,915 discloses catalysts

15   comprising phosphorus, vanadium and oxygen, and a promoter component containing each of iron and lithium which are useful for the partial oxidation of nonaromatic hydrocarbons, particularly n-butane, with molecular oxygen or a molecular oxygen-containing gas

20   in the vapor phase to produce maleic anhydride in excellent yields.

       U.S. Patent No. 4,562,268 relates to a process for the production of maleic anhydride from nonaromatic hydrocarbons in the presence of a

25   vanadium/phosphorus mixed oxide oxidation catalyst wherein the catalyst exhibits a single pass weight/-weight productivity of at least 70 grams of maleic anhydride per kilogram of catalyst per hour.

       U.S. Patent No. 4,333,853 discloses a

30   vanadium/phosphorus mixed oxide catalyst prepared by reducing vanadium substantially in the pentavalent valence state to a tetravalent valence state in the presence of a phosphorus-containing compound and in the absence of a corrosive reducing agent in an

35   organic liquid medium capable of reducing the vanadium to a valence state less than +5, recovering the resultant vanadium/phosphorus mixed oxide catalyst precursor, drying such precursor, and calcining the

precursor to obtain the active catalyst. Such
catalysts reportedly are effective in the oxidation of
C_4 hydrocarbons such as n-butane, 1- and 2-butenes,
1,3-butadiene, or mixtures thereof to produce maleic
anhydride with selectivities ranging from 58.7% to
68.1% and yields (mol %) ranging from 51.4% to 59.5%.

U.S. Patent No. 4,315,864 relates to a process
for the production of maleic anhydride from normal C_4
hydrocarbons in the presence of a vanadium/phosphorus
mixed oxide catalyst. The catalyst is prepared by
reducing a pentavalent vanadium-containing compound in
an olefinic, oxygenated organic liquid medium to a +4
valence in the absence of a corrosive reducing agent,
recovering resultant catalyst precursor, drying the
catalyst precursor, and calcining the precursor to
obtain the active catalyst.

U.S. Patent No. 4,312,787 describes a catalyst
which comprises an inert support and a catalytically
active mixed oxide material coating of vanadium and
phosphorus or of vanadium, phosphorus, and uranium on
the outer surface of the support in an amount greater
than 50% to about 80% by weight of the combined
support and oxide material. Catalysts within the
scope of the claims of the patent were reported to
produce maleic anhydride from n-butane in yields
ranging from 53% to 62.5%, with selectivities ranging
from 57.4% to 67.9%.

In U.S. Patent No. 4,251,390, a zinc-promoted
vanadium-phosphorus-oxygen catalyst is disclosed and
claimed. The catalyst is prepared by reducing
pentavalent vanadium in a substantially anhydrous
organic medium to a lower valent state and digesting
the reduced vanadium in the presence of a zinc
promoter compound. The resultant catalyst is
activated by bringing the catalyst to operating
temperatures for the oxidation of n-butane to maleic
anhydride at a rate of 5° C to 10° C per hour in the
presence of a butane-in-air mixture.

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In U.S. Patent No. 4,187,235, a process is
described for preparing maleic anhydride from n-butane
in the presence of a vanadium-phosphorus-oxygen high
surface area catalyst, that is, 10 to 100 square
5 meters per gram (m^2/g), as determined by the BET
method. The catalyst is prepared by reducing
pentavalent vanadium to a valence between +4.0 and
+4.6 with a substantially anhydrous primary or
secondary alcohol and contacting the reduced vanadium
10 with phosphoric acid, followed by recovering and
calcining the resultant vanadium(IV) phosphate
compound.

U.S. Patent 4,018,709 discloses a process for the
vapor phase oxidation of normal C_4 hydrocarbons using
15 catalysts containing vanadium, phosphorus, uranium, or
tungsten or a mixture of elements from zinc, chromium,
uranium, tungsten, cadmium, nickel, boron, and
silicon. In a preferred embodiment, the catalyst also
contains an alkali metal or an alkaline earth metal,
20 especially lithium, sodium, magnesium, or barium as
active components. Typically, such catalysts are
prepared in concentrated (37%) hydrochloric acid.

In U.S. Patent No. 3,980,585, a process is
disclosed for the preparation of maleic anhydride from
25 normal C_4 hydrocarbons in the presence of a catalyst
containing vanadium, phosphorus, copper, oxygen,
tellurium, or a mixture of tellurium and hafnium or
uranium or a catalyst containing vanadium, phosphorus,
copper, and at least one element selected from the
30 group of tellurium, zirconium, nickel, cerium,
tungsten, palladium, silver, manganese, chromium,
zinc, molybdenum, rhenium, samarium, lanthanum,
hafnium, tantalum, thorium, cobalt, uranium, and tin,
optionally (and preferably) with an element from
35 Groups IA (alkali metals) or IIA (alkaline earth
metals).

U.S. Patent No. 3,888,866 discloses a process for
the oxidation of n-butane at a temperature from about

300° C to about 600° C with a vanadium/phosphorus/
oxygen catalyst having a phosphorus/vanadium atom
ratio of 0.5-2, promoted or modified with chromium,
iron, hafnium, zirconium, lanthanum, and cerium, the

5 promoter metal/vanadium atom ratio being between about
0.0025 and about 1. The catalysts are prepared by
refluxing a reaction mixture of vanadium oxide,
phosphorus, a hydrogen halide (usually hydrochloric
acid), and a specified promoter metal-containing

10 compound. The resultant catalyst precursors are
recovered, dried, formed into structures -- spheres,
for example -- and calcined to produce the active
catalyst.
        U.S. Patent No. 3,864,280 discloses

15 vanadium/phosphorus mixed oxide catalyst having an
intrinsic surface area of from about 7 to about 50
m^2/g. The catalysts are prepared by precipitation of a
vanadium/phosphorus/oxygen complex from an essentially
organic solvent medium in the absence of gross amounts

20 of water. The resultant crystalline precipitate is
activated by heating in air, followed by a 1.5 mol %
butane-in-air mixture, both at elevated temperatures.
        U.S. Patent No. 3,862,146 discloses a process for
the oxidation of n-butane to maleic anhydride in the

25 presence of a vanadium-phosphorus-oxygen catalyst
complex, promoted or activated with zinc, bismuth,
copper, or lithium activator. The phosphorus/vanadium
and activator/vanadium atom ratios are from about 0.5-
5 and from about 0.05-0.5, respectively.

30   U.S. Patent No. 3,856,824 discloses a process for
the production of maleic anhydride by oxidation of
saturated aliphatic hydrocarbons in the presence of a
catalyst comprising vanadium, phosphorus, iron,
oxygen, and added modifier comprising chromium

35 combined with at least one element selected from the
group consisting of nickel, boron, silver, cadmium,
and barium.

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European Patent Application No. 98,039 discloses
a process for the preparation of vanadium-phosphorus
mixed oxide catalysts, optionally containing an added
promoter element selected from the group consisting of
5 Group IA (alkali metals), Group IIA (alkaline earth
metals), titanium, chromium, tungsten, niobium,
tantalum, manganese, thorium, uranium, cobalt,
molybdenum, iron, zinc, hafnium, zirconium, nickel,
copper, arsenic, antimony, tellurium, bismuth, tin,
10 germanium, cadmium, and lanthanides, and mixtures
thereof. The catalysts, which exhibit a
phosphorus/vanadium atom ratio of from about 0.8 to
about 1.3 and a promoter/vanadium atom ratio from
about 0.01 to about 0.5, are prepared in an organic
15 liquid reaction medium capable of reducing the
vanadium to a valence state of approximately +4 to
form a nonsolubilized catalyst precursor, contacting
the nonsolubilized catalyst precursor-containing
organic liquid with water to form a two-phase system
20 having an upper organic liquid phase and a lower
nonsolubilized catalyst precursor-containing aqueous
phase, drying the catalyst precursor, and calcining
the precursor to obtain the active catalyst.
     The oxidation catalysts described in the cited
25 references disclose several well-known solid catalyst
shapes commonly employed in fixed-bed vapor phase
maleic anhydride production processes, for example,
spheres or spheroids, tablets, and pellets. And
although the prior art catalysts and catalyst shapes
30 generally are successful in producing the desired
maleic anhydride product, the commercial utility of a
catalyst system and a catalytic process is highly
dependent upon the cost of the catalyst employed, the
conversion of the reactants, and the yield of the
35 desired product(s), or stated differently, the actual
productivity of the catalyst system. In many
instances, a reduction in the cost of a catalyst
system employed in a given catalytic process on the

order of a few cents per kilogram or pound, or a small
percent increase in the yield of the desired product,
relative to the amount of catalyst required,
represents a tremendous economic advantage in a
5   commercial operation. Accordingly, research efforts
are continually being made to define new or improved
catalyst systems and methods and processes of making
new and old catalyst systems to reduce the cost and/or
upgrade the activity, selectivity, and/or productivity
10 of such catalyst systems in such catalytic processes.
The discovery of the shaped oxidation catalyst
structures of the instant invention, therefore, is
believed to be a decided advance in the art.

BRIEF DESCRIPTION OF THE DRAWINGS

15   FIG. 1A illustrates a solid cylindrical structure
with void spaces as equally spaced rounded grooves
disposed in the external surface, running
substantially vertically from top to bottom.

FIG. 1B illustrates, in top elevational view, a
20 solid cylindrical structure with void spaces as
equally spaced rounded grooves disposed in the exter-
nal surface, running substantially vertically from top
to bottom.

FIG. 2A illustrates a variation of the structure
25 illustrated in FIG. 1A with void spaces as equally
spaced rounded grooves disposed in the external
surface, running substantially vertically from top to
bottom.

FIG. 2B illustrates, in top elevational view, a
30 variation of the structure illustrated in FIG. 1B with
void spaces as equally spaced rounded grooves disposed
in the external surface, running substantially
vertically from top to bottom.

FIG. 3A illustrates a solid cylindrical structure
35 with void spaces as equally spaced rounded grooves
disposed in the external surface and a centrally
located bore.

FIG. 3B illustrates, in top elevational view, a solid cylindrical structure with void spaces as equally spaced rounded grooves disposed in the external surface and a centrally located bore.

5   FIG. 4A illustrates a solid cylindrical structure with a void space as a centrally located bore.

FIG. 4B illustrates, in top elevational view, a solid cylindrical structure with a void space as a centrally located bore.

10   FIG. 5A illustrates a solid cylindrical structure with void spaces as equally spaced angular grooves disposed in the external surface, running substantially vertically from top to bottom.

FIG. 5B illustrates, in top elevational view, a
15 solid cylindrical structure with void spaces as equally spaced angular grooves disposed in the external surface, running substantially vertically from top to bottom.

FIG. 6A illustrates a solid cylindrical structure
20 with a void space as a continuous angular spiral disposed in the external surface running from top to bottom.

FIG. 6B illustrates, in top elevational view, a solid cylindrical structure with a void space as a
25 continuous angular spiral disposed in the external surface running from top to bottom.

FIG. 7A illustrates a solid cylindrical structure with a void space as a rounded groove disposed in the external surface in communication with a centrally
30 located bore.

FIG. 7B illustrates, in top elevational view, a solid cylindrical structure with a void space as a rounded groove disposed in the external surface in communication with a centrally located bore.

35   FIG. 8A illustrates a solid square-based pyramidal structure with void spaces as equally spaced rounded grooves disposed in the external surface at the corner edges.

FIG. 8B illustrates, in top elevational view, a solid square-based pyramidal structure with void spaces as equally spaced rounded grooves disposed in the external surface at the corner edges.

5   FIG. 9A illustrates a solid square-based pyramidal structure with void spaces as equally spaced rounded grooves disposed in the external surface at the sides, running along the sloping sides from top to bottom.

10   FIG. 9B illustrates, in top elevational view, a solid square-based pyramidal structure with void spaces as equally spaced rounded grooves disposed in the external surface at the sides, running along the sloping sides from top to bottom.

15   FIG. 10A illustrates a solid conical structure with void spaces as equally spaced rounded grooves disposed in the external surface, running along the sloping sides from top to bottom.

FIG. 10B illustrates, in top elevational view, a

20   solid conical structure with void spaces as equally spaced rounded grooves disposed in the external surface, running along the sloping sides from top to bottom.

FIG. 11A illustrates a solid cubical structure

25   with void spaces as equally spaced angular grooves disposed in the external surface at the sides, running substantially vertically from top to bottom.

FIG. 11B illustrates, in top elevational view, a solid cubical structure with void spaces as equally

30   spaced angular grooves disposed in the external surface at the sides, running substantially vertically from top to bottom.

FIG. 12A illustrates a solid cubical structure with void spaces as equally spaced angular grooves

35   disposed in the external surface at the sides, running substantially vertically from top to bottom.

FIG. 12B illustrates, in top elevational view, a solid cubical structure with void spaces as equally

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spaced angular grooves disposed in the external
surface at the sides, running substantially vertically
from top to bottom.

FIG. 13A illustrates a solid cubical structure
5   with void spaces as equally spaced rounded dimples
disposed in the external surface at the sides, top,
and bottom.

FIG. 13B illustrates, in top elevational view, a
solid cubical structure with void spaces as equally
10 spaced rounded dimples disposed in the external
surface at the sides, top, and bottom.

FIG. 14A illustrates a solid spherical structure
with void spaces as equally spaced rounded dimples
disposed in the external surface.

15   FIG. 14B illustrates, in cross sectional view at
the equator, a solid spherical structure with void
spaces as equally spaced rounded dimples disposed in
the external surface.

SUMMARY OF THE INVENTION

20   This invention is directed to shaped oxidation
catalyst structures. Accordingly, the primary object
of this invention is to provide shaped oxidation
catalyst structures containing catalytic material
comprised of mixed oxides of vanadium and phosphorus
25 which are suitable for the production of maleic
anhydride via the partial oxidation of nonaromatic
hydrocarbons in the vapor phase with molecular oxygen
or a molecular oxygen-containing gas, the use of which
results in enhanced catalyst activity, as determined
30 by weight/weight productivity, when compared to
conventional oxidation catalyst shapes for the
production of maleic anhydride.

This and other objects, aspects, and advantages
of the instant invention will become apparent to those
35 skilled in the art from the accompanying description
and claims.

The above objects are achieved by the shaped
oxidation catalyst structures of the instant invention

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which comprise a solid geometric form having at least
one (1) void space disposed in the external surface
thereof, the shaped structure being characterized by
(a) containing catalytic material comprised of mixed
5   oxides of vanadium and phosphorus, and (b) exhibiting
(i) a geometric volume of from about 30 percent to
about 90 percent of that exhibited by the void space-
free solid geometric form, (ii) an external geometric
surface area/geometric volume ratio of at least about
10 15 cm^{-1}, (iii) a bulk density of from about 0.4 gram
per cubic centimeter (g/cm^3) to about 1.4 g/cm^3, and
(iv) a mechanical resistance sufficient to maintain
substantially the structural integrity of the shaped
structure under handling and use conditions.

15   DESCRIPTION OF THE PREFERRED EMBODIMENTS
         In accordance with this invention, shaped
oxidation catalyst structures are provided for the
production of maleic anhydride by the partial
oxidation of nonaromatic hydrocarbons in the vapor
20 phase with molecular oxygen or a molecular oxygen-
containing gas. The shaped structures comprise a
solid geometric form having at least one (1) void
space disposed in the external surface thereof. In
addition, such shaped structures are characterized by
25 a combination of properties effective to demonstrate
enhanced catalyst activity, as determined by weight/-
weight productivity, when compared to conventional
oxidation catalyst shapes for the production of maleic
anhydride.
30   For purposes of this invention, the term "void
space" means the unoccupied space in the solid
geometric form other than pores and crevices which
normally are present in a solid geometric form
catalyst structure. The term "weight/weight produc-
35 tivity" means the weight of maleic anhydride (MAN) ex-
pressed in grams produced during a single pass of
hydrocarbon feedstock over the catalyst per unit of
weight of catalyst expressed in kilograms per unit of

time expressed in hours, the term expressed as g .
maleic anhydride/kg catalyst-hour or g MAN/kg cat.-
hr. The term "yield" means (a) the ratio of the moles
of maleic anhydride obtained to the moles of

5 hydrocarbon feedstock introduced into the reactor
multiplied by 100, the term expressed as mol %, and
(b) the ratio of the weight of maleic anhydride
obtained to the weight of hydrocarbon feedstock intro-
duced into the reactor multiplied by 100, the term

10 expressed as weight % or wt %. The term "selectivity"
means the ratio of moles of maleic anhydride obtained
to the moles of hydrocarbon reacted or converted
multiplied by 100, the term expressed as mol %. The
term "conversion" means the ratio of moles of

15 hydrocarbon feedstock reacted to the moles of
hydrocarbon introduced into the reactor multiplied by
100, the term expressed as mol %. The term "space
velocity" or "gas hourly space velocity" or "GHSV"
means the hourly volume of gaseous feed expressed in

20 cubic centimeters (cm^3) .at 20° C and atmosphere
pressure, divided by the catalyst bulk volume,
expressed as cm^3/cm^3/hour or hr^{-1}.

The solid geometric forms suitable to represent
base structures of the shaped oxidation catalyst

25 structures of the instant invention include any solid
geometric in which void spaces can be disposed in the
external surface thereof to provide the shaped
oxidation catalyst structures of the instant
invention. Nonlimiting exemplary solid geometric

30 forms include cylinders, cubes, cones, truncated
cones, pyramids, truncated pyramids, spheres, prisms,
and the like.

A critical feature of the instant invention is
the disposition of void spaces in the external surface

35 of the solid geometric form. Suitable void spaces
include grooves, holes, dimples, and the like. The
void spaces are in general equally spaced or
distributed over the external surface in which such

void spaces are located. The number and shape of the
void spaces disposed in the external surface of the
solid geometric form is not narrowly critical. All
that is necessary is that the resultant shaped

5   oxidation catalyst structure exhibits certain charac-
terizing properties as hereinafter discussed.
Accordingly, the shape of the corners of the void
spaces, as well as any protrusions associated
therewith, may be angular or rounded and the number of

10 such void spaces, which must be at least one (1), may
be any practical number, taking into consideration the
dimensions of the void spaces and the available
external geometric surface in which they are disposed.
In general, it is preferred to have the shape of the

15 corners rounded.

In connection with the disposition of void spaces
in the external surface of the solid geometric form,
the geometric volume of the shaped oxidation catalyst
structures, of necessity, must be reduced to a value

20 less than that of the void space-free solid geometric
form. In accordance with the instant invention, the
shaped oxidation catalyst structures of the instant
invention must exhibit a geometric volume of from
about 30 percent to about 90 percent, preferably from

25 about 40 percent to about 80 percent, of that ex-
hibited by the void space-free geometric form. The
retention of such geometric volume, in combination
with other characterizing properties of the shaped
oxidation catalyst structures of the instant

30 invention, results in such structures exhibiting
enhanced catalyst activity, as determined by weight/-
weight productivity, when compared to conventional
oxidation catalyst shapes, including corresponding
void space-free solid geometric forms, for the

35 production of maleic anhydride.

The shaped oxidation catalyst structures of the
instant invention exhibit a characteristic geometric
volume and geometric surface area as a consequence of

the cross-sectional shape and dimensions associated
therewith. The geometric volume and geometric surface
area are readily calculated from appropriate
measurements associated with the corresponding perfect

5   geometric forms. The shaped oxidation catalyst struc-
tures of the instant invention closely approximate
such forms and their geometric surface areas and
geometric volumes can be closely estimated from the
corresponding geometric models. The (external)

10 geometric surface area/geometric volume ratio
advantageously is at least 15 cm^{-1}, preferably at least
about 20 cm^{-1}.

    The bulk density of the shaped oxidation catalyst
structures is indicative of the amount or quantity of

15 catalyst material contained in a specified catalyst
shape. It will be apparent, of course, for a shaped
structure having specified dimensions, the greater the
amount of catalyst material (or material in general,
regardless of whether the material is catalyst

20 material or a combination of catalyst material and
filler or inert material) contained therein, the
greater will be the bulk density. On the other hand,
with everything else being equal, the greater the bulk
density, the more tightly packed is the material

25 contained therein. This, in turn, is accompanied by a
decrease in porosity, thereby inhibiting the movement
of reactant gas molecules into and out of the shaped
catalyst structure. The shaped oxidation catalyst
structures of the instant invention, however, do not

30 suffer from this difficulty in that such structures
exhibit a bulk density of from about 0.4 g/cm^3 to about
1.4 g/cm^3, preferably from about 0.5 g/cm^3 to about 1.1
g/cm^3.

    It will be apparent to those skilled in the art

35 that the shaped oxidation catalyst structures must
possess sufficient mechanical resistance or physical
strength to withstand handling, transportation from
the source of manufacture to the reactor in which it

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is to be used, and charging into the reactor. In
addition, the shaped structures must be able to
support their own weight in the reactor. Or stated
differently, the shaped oxidation catalyst structures
5   must possess mechanical resistance sufficient to
maintain substantially the structural integrity of the
shaped structure under handling and use conditions.
If the shaped structures has insufficient mechanical
resistance, crushing of the shaped structure can
10   result. This, in turn, results in adverse economic
consequences such as increased pressure drop and
decreased reactant gas flow rates, increased costs for
production of the shaped oxidation catalyst structures
due to yield losses to fines and broken pieces, and
15   less efficient reactor operation due to hot spots in
the catalyst bed. In general, sufficient mechanical
resistance, as determined by side crush strength
measurements -- the amount of pressure required to
break or crush the shaped structure -- exists for
20   structures exhibiting a side crush strength of from
about 4.45 newtons (N) to about 222.4 N (about 1 lb to
about 50 lb), preferably from about 13.3 N to about 89
N (3 lb to about 20 lb). Or stated differently, the
mechanical resistance of the shaped structure is
25   sufficient to maintain substantially the structural
integrity thereof, while at the same time is not
excessive to the point that the porosity of the shaped
structure is reduced to a value such that the movement
of reactant gas molecules into and out of the shaped
30   structure is inhibited.
        The shaped oxidation catalyst structures of the
instant invention may have any practical size and
dimensions, taking into account the overall dimensions
of the particular reactor tube in which they are to be
35   used. In general, a base width (that is, the widest
portion of the structure) of from about 3.175 mm to
about 6.35 mm and a height-to-base width ratio of from
about 0.5 to about 2.0 are advantageously employed.

Catalyst materials suitable for use in the
instant invention are those known to the art, and in
general are materials capable of catalyzing the vapor
phase partial oxidation of hydrocarbons to maleic
5   anhydride under oxidation conditions. Such materials
in general comprise a vanadium phosphorus oxide
complex, optionally further comprising a promoter
element. A convenient, albeit nonlimiting,
representation of an empirical formula for suitable
10   catalytic material may be expressed as $VP_xO_yM_z$ wherein
M is at least one promoter element selected from the
group consisting of elements from Groups IA, IB, IIA,
IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIB, and VIIIB of
the Periodic Table of the Elements, x is a number from
15   about 0.5 to about 2.0, preferably from about 0.95 to
about 1.35, y is a number taken to satisfy the
valences of V, P, and M in the oxidation states in
which they exist in the composition, and z is a number
from zero (0) to about 1.0, preferably up to about
20   0.5.

Specific, albeit nonlimiting, examples of
suitable catalyst materials are those described in
several of the references previously noted in the
"Description of the Prior Art" -- U.S. Patent Nos.
25   4,632,915; 4,562,268; 4,333,853; 4,315,864; 4,312,
787; 4,251,390; 4,187,235; 4,018,709; 3,980,585;
3,888,866; 3,864,280; 3,862,146; and 3,856,824; and
European Patent Application No. 98,039 -- it being
understood, however, that the same are not to be
30   construed as limiting but instead are for purposes of
illustration and guidance in the practice of the
instant invention. These references are herein
incorporated by reference. Among such catalyst
materials, those in general preferred for use in the
35   instant invention are those described in U.S. Patent
Nos. 4,632,915 and 4,562,268.

The shaped oxidation catalyst structures of the
instant invention may be prepared by blending the

catalyst material with shaped structure forming aids
known to the art such as graphite or stearic acid and
any desirable inert filler material and pressing or
compacting in a mold (tableting press equipped with an
5   appropriate die and punch) or by extrusion or casting
in accordance with procedures known in the art. In
general, the compaction technique is preferred in that
shaped structures exhibiting characterizing properties
in accordance with the instant invention are more
10   readily obtained. In a similar manner, the absence of
the employment of inert filler material is preferred
in that the partial oxidation reaction of hydrocarbon
to maleic anhydride is advantageously carried out in a
manner which maximizes the amount of active catalyst
15   material contained in the specified volume of the
reactor to thereby maximize the amount of hydrocarbon
converted in a single reactor pass.

The shaped oxidation catalyst structures of the
instant invention are useful in a variety of reactors
20   to convert nonaromatic hydrocarbons to maleic
anhydride. A typically satisfactory reactor is a heat
transfer medium-cooled fixed bed tube-type reactor.
The details of operation of such reactors are well
known to those skilled in the art. The tubes of such
25   reactors can be constructed of iron, stainless steel,
carbon steel, nickel, glass, such as Vycor, and the
like and can vary in diameter from about 0.635 cm
(0.25 in.) to about 3.81 cm (1.50 in.) and the length
can vary from about 15.24 cm (6 in.) to about 762 cm
30   (25 ft). The oxidation reaction is highly exothermic
and once reaction is underway, in order to maintain
the desired reactor temperature, a heat transfer
medium is necessary to conduct heat away from the
reactor. Suitable heat transfer media are well known
35   to those skilled in the art and, in general, are
materials that remain in the liquid state at process
temperatures and have a relatively high thermal
conductivity. Examples of useful media include

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various heat transfer oils, molten sulfur, mercury,
molten lead, and salts such as nitrates and nitrites
of alkali metals, the salts being preferred due to
their high boiling points. A particularly preferred
5   heat transfer medium is a eutectic mixture of
potassium nitrate, sodium nitrate and sodium nitrite
which not only has a desirably high boiling point, but
also, a sufficiently low freezing point that it
remains in a liquid state even during periods of
10   reactor shutdown. An additional method of temperature
control is to use a metal block reactor whereby the
metal surrounding the reaction zone of the reactor
acts as a temperature regulating body or by
conventional heat exchangers.
15   In general, the reaction to convert nonaromatic
hydrocarbons to maleic anhydride using the shaped
oxidation catalyst structures of the instant invention
involves charging a mixture of a nonaromatic hydrocar-
bon having at least four (4) carbon atoms in a
20   straight chain (or in a cyclic structure) and a
molecular oxygen-containing gas (including molecular
oxygen, itself), such as air or molecular oxygen-
enriched air, to a heat transfer medium-cooled reactor
or reaction zone packed with the shaped oxidation
25   catalyst structures of the instant invention to
contact the hydrocarbon/molecular oxygen-containing
gas mixture with the catalyst at elevated tempera-
tures. In addition to the hydrocarbon and molecular
oxygen, other gases, such as nitrogen or steam, may be
30   present or added to the reactant feedstream.
Typically, the hydrocarbon is admixed with the
molecular oxygen-containing gas, preferably air, at a
concentration of from about 1 mol % to about 10 mol %
hydrocarbon and contacted with the catalyst at a gas
35   hourly space velocity (GHSV), or simply space
velocity, of from about 100 hr^{-1} up to about 5,000 hr^{-1}
and at a temperature of from about 300° C to about
600° C, preferably from about 1,000 hr^{-1} to about 3,000

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hr^{-1} and from about 325° C to about 500° C to produce
maleic anhydride.

The initial yield of maleic anhydride, however,
may be low. And if this is the case, the catalyst, as
5   will occur to those skilled in the art, can be
"conditioned" by contacting the shaped oxidation
catalyst structures of the instant invention with low
concentrations of hydrocarbon and molecular oxygen-
containing gas at low space velocities for a period of
10   time before production operations begin.

Pressure is not critical in the reaction to
convert nonaromatic hydrocarbons to maleic anhydride.
The reaction may be conducted at atmospheric,
superatmospheric, or subatmospheric pressure. It
15   generally will be preferred, however, for practical
reasons, to conduct the reaction at or near
atmospheric pressure. Typically, pressures of from
about 1.013 x 10^2 kilopascals-gauge (kPa-g, 14.7 psig,
1 atm) to about 3.45 x 10^2 kPa-g (50.0 psig),
20   preferably from about 1.24 x 10^2 kPa-g (18.0 psig) to
about 2.068 x 10^2 kPa-g (30.0 psig), may be
conveniently employed.

Maleic anhydride produced by using the shaped
oxidation catalyst structures of the instant invention
25   can be recovered by any means known to those skilled
in the art. For example, maleic anhydride can be
recovered by direct condensation or by absorption in
suitable media with subsequent separation and
purification of the maleic anhydride.

30   For purposes of comparing the efficiency, as
determined by weight/weight productivity and maximum
reaction yield, of the shaped oxidation catalyst
structures of the instant invention with oxidation
catalyst structures not within the scope of the
35   instant invention, the weight/weight productivity and
maximum reaction yield values are determined by
carrying out the maleic anhydride production at
standardized conditions. And although any

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standardized set of conditions can be employed to
establish weight/weight productivity and maximum
reaction yield values, the values reported herein were
determined at a hydrocarbon-in-air concentration of

5   1.5 mol % and 2,000 hr^{-1} while adjusting the
hydrocarbon conversion to a value, typically from
about 70 mol % to about 90 mol %, sufficient to
provide the highest possible yield of maleic
anhydride. It will be recognized, of course, that

10   while weight/weight productivity and maximum reaction
yield values, as reported herein, are determined at
the previously stated standardized conditions, other
conditions may be employed, if desired. However,
weight/weight productivity and maximum reaction yield

15   values determined at conditions other than 1.5 mol %
hydrocarbon-in-air concentration and 2,000 hr^{-1} space
velocity while adjusting the hydrocarbon conversion to
a value sufficient to provide the highest possible
yield of maleic anhydride generally will differ from

20   those determined at the standardized conditions
employed herein. As a result, direct comparison of
weight/weight productivity and maximum reaction values
for different catalyst structures may be made only if
such values are determined under the same standardized

25   conditions.

A large number of nonaromatic hydrocarbons having
from four to 10 carbon atoms can be converted to
maleic anhydride using the shaped oxidation catalyst
structures of the instant invention. It is only

30   necessary that the hydrocarbon contain not less than
four carbon atoms in a straight chain or in a cyclic
ring. As an example, the saturated hydrocarbon n-
butane is satisfactory, but isobutane (2-methyl-
propane) is not satisfactory for conversion to maleic

35   anhydride although its presence is not harmful. In
addition to n-butane, other suitable saturated
hydrocarbons include the pentanes, the hexanes, the
heptanes, the octanes, the nonanes, the decanes, and

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mixtures of any of these, with or without n-butane, so
long as a hydrocarbon chain having at least four
carbon atoms in a straight chain is present in the
saturated hydrocarbon molecule.

5   Unsaturated hydrocarbons are also suitable for
conversion to maleic anhydride using the shaped
oxidation catalyst structures of the instant
invention. Suitable unsaturated hydrocarbons include
the butenes (1-butene and 2-butene), 1,3-butadiene,
10   the pentenes, the hexenes, the heptenes, the octenes,
the nonenes, the decenes, and mixtures of any of
these, with or without the butenes, again, so long as
the requisite hydrocarbon chain having at least four
carbon atoms in a straight chain is present in the
15   molecule.

Cyclic compounds such as cyclopentane and
cyclopentene also are satisfactory feed materials for
conversion to maleic anhydride using the shaped
oxidation catalyst structures of the instant
20   invention.

Of the aforementioned feedstocks, n-butane is the
preferred saturated hydrocarbon and the butenes are
the preferred unsaturated hydrocarbons, with n-butane
being most preferred of all feedstocks.

25   It will be noted that the aforementioned
feedstocks need not necessarily be pure substances,
but can be technical grade hydrocarbons.

The principal product from the oxidation of the
aforementioned suitable feed materials is maleic
30   anhydride, although small amounts of citraconic
anhydride (methyl maleic anhydride) also may be
produced when the feedstock is a hydrocarbon contain-
ing more than four carbon atoms.

The following specific examples illustrating the
35   best currently-known method of practicing this
invention are described in detail in order to
facilitate a clear understanding of the invention. It
should be understood, however, that the detailed

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expositions of the application of the invention, while
indicating preferred embodiments, are given by way of
illustration only and are not to be construed as
limiting the invention since various changes and
5   modifications within the spirit of the invention will
become apparent to those skilled in the art from this
detailed description.

<u>EXAMPLE 1</u>

A twelve-liter, round bottom flask, fitted with a
10   paddle stirrer, a thermometer, a heating mantle, and a
reflux condenser, was charged with 9,000 mL of
isobutyl alcohol, 378.3 g (4.20 mol) of oxalic acid
($C_2H_2O_4$), and 848.4 g (4.66 mol) of vanadium pentoxide
(V_2O_5). To this stirred mixture was added 997.6 g
15   (10.76 mol) of phosphoric acid (H_3PO_4, 105.7 % by
weight). The resultant mixture was refluxed for about
16 hours to give a bright blue mixture. After
stripping off 6 L of isobutyl alcohol over a 3-hour
period, the mixture was cooled and quantitatively
20   transferred to a flat porcelain dish and dried for 48
hours at 110° C in nitrogen, followed by 48 hours at
150° C in air. The dried material was transferred to
another box oven and heated in air at 250-260° C for
approximately one hour to yield a grey-black catalyst
25   precursor powder.

The catalyst precursor powder was blended to
contain approximately four (4.0) weight % graphite and
compressed on a Stokes 512 Rotary Tableting machine
equipped with appropriate dies and punches to produce
30   the desired shaped catalyst structure, 1.27 cm
cylinders with a tablet density of 1.30-1.50 g/cm^3.
The 1.27 cm slugs were ground to produce a tablet feed
powder in the size range of from 18 mesh [U.S.
Standard Sieve Size, 1.00 millimeter (mm)] to 30 mesh
35   (600 microns, μm) and fed into the tableting machine
equipped with appropriate dies and punches to produce
the shaped catalyst structure of interest. The
compaction pressure was adjusted to produce structures

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with average (side) crush strengths of from 13.3 N to
89 N (3 lb to 20 lb). The characterizing properties
of the shaped catalyst structures produced are sum-
marized in Table 1.

5   Each of the shaped catalyst structures produced
was activated. The shaped catalyst structure was
placed onto a 30.48 cm x 30.48 cm x 2.54 cm tray
formed from stainless steel mesh screen having
approximately 40% open area. The tray was transferred
10   to an air-purged box oven that previously had been
heated to approximately 425° C. This temperature was
maintained for a period of time from approximately one
hour to about two hours. Thereafter, the tray of
shaped catalyst structures was removed from the oven
15   and cooled. The tray of shaped catalyst structures
were then transferred to a box oven purged with
nitrogen gas and heated to approximately 275° C, at
which temperature the atmosphere in the oven was
changed to a mixture of approximately 50 % by volume
20   nitrogen and 50 % by volume steam. The temperature
was raised over a period of from one hour to two hours
to approximately 425° C and maintained at such
temperature for approximately six hours. The tray of
shaped catalyst structures was then allowed to cool to
25   room temperature (approximately 25° C) while purging
the oven with dry nitrogen. The shaped catalyst
structures were charged to a 2.10 cm inside diameter x
121.9 cm long fixed bed tubular reactor and
performance tested as described in Example 5, below.

30   EXAMPLE 2
          This example illustrates the preparation of a
vanadium phosphorus oxide in accordance with the
procedure described for Examples 1-7 of U. S. Patent
No. 4,333,853.

35   A twelve-liter, round bottom flask equipped as
described in Example 1, above, was charged with 7,340
mL of isobutyl alcohol and 513.5 g (2.82 mol) of V_2O_5.
Stirring was begun and a solution of 663.97 g (6.78

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mol) of 100% H_3PO_4 in 1129 mL of isobutyl alcohol. The
resultant mixture was then refluxed for about 16 hours
to give a light blue mixture. The mixture was cooled
and the precipitate was filtered and the precipitate
5   dried at ambient temperatures under vacuum. The dried
precipitate thereafter was washed with approximately
1200 mL of isobutyl alcohol, followed by drying at
145° C for approximately 2.5 hours, and calcining for
approximately one hour in air at 400° C.

10   The catalyst precursor powder was blended to
contain approximately 2.54 weight % stearic acid and
fed into a Stokes 512 Rotary Tableting machine
equipped with appropriate dies and punches to produce
the desired shaped catalyst structure. The compac-
15   tion pressure was adjusted to produce structures with
average (side) crush strengths of from 13.3 N to 89 N
(3 lb to 20 lb). The characterizing properties of the
shaped catalyst structures produced are summarized in
Table 1. The thusly prepared shaped catalyst struc-
20   tures were charged to a 2.10 cm inside diameter x
121.9 cm long (0.83 in. inside diameter x 4 ft long)
fixed bed tubular reactor and performance tested as
described in Example 5, below.

<u>EXAMPLE 3</u>

25   This example illustrates the preparation of a
lithium/zinc-promoted vanadium phosphorus oxide
catalyst in accordance with the procedure described
for Examples 1-7 of U. S. Patent No. 4,333,853.

A twelve-liter, round bottom flask equipped as
30   described in Example 1, above, except that it was
further equipped with a Dean Stark trap and a gas
dispersion tube, was charged with 6,500 mL of isobutyl
alcohol and 1145.0 g (6.29 mol) of V_2O_5. Stirring was
begun and dry hydrogen chloride (HCl) was passed into
35   the stirred mixture at a rate sufficient to maintain
the reaction temperature at approximately 50° C.
After 6 hours and 43 minutes of HCl addition a dark
reddish brown solution resulted. To this solution was

added a solution containing 1089.5 g (9.51 mol) of
85.5% H_3PO_4, 422.0 g (2.97 mol) of phosphorus pentoxide
(P_2O_5) dissolved in 1500 mL of isobutyl alcohol. An
additional 100 mL of isobutyl alcohol was used to

5   rinse the phosphorus-containing solution into the
vanadium-containing solution. Zinc chloride ($ZnCl_2$,
17.17 g, 0.13 mol) and 1.07 g (0.025 mol) of lithium
chloride (LiCl) were then added to the reaction
solution. The resultant solution was heated to reflux

10   and refluxed for approximately two (2) hours, followed
by stripping off of 5.33 L of isobutyl alcohol over a
period of four (4) hours. The mixture was cooled and
quantitatively transferred to a porcelain dish and
dried at 150° C.

15   The catalyst precursor powder was blended to
contain approximately four (4.0) weight % graphite and
compressed on a Stokes 512 Rotary Tableting machine
equipped with appropriate dies and punches to produce
the desired shaped catalyst structure, 1.27 cm

20   cylinders with a tablet density of approximately 1.90
g/cm³. The 1.27 cm slugs were ground to produce a
tablet feed powder in the size range of from 18 mesh
(U.S. Standard Sieve Size, 1.00 mm) to 30 mesh (600
μm) and fed into the tableting machine equipped with

25   appropriate dies and punches to produce the shaped
catalyst structure of interest. The compaction
pressure was adjusted to produce structures with
average (side) crush strengths of from 13.3 N to 89 N
(3 lb to 20 lb). The characterizing properties of the

30   shaped catalyst structures produced are summarized in
Table 1. The thusly prepared shaped catalyst struc-
tures were activated according to the activation
procedure described in U.S. Patent No. 4,333,853 by
charging the structures to a 2.10 cm inside diameter x

35   121.9 cm long (0.83 in. inside diameter x 4 ft long)
fixed bed tubular reactor. The reactor was warmed
slowly to 400° C while passing a gas stream
containing 0.5-0.7 mol % n-butane in air over the

shaped catalyst structures, beginning at approximately
280° C. After the temperature had reached 400° C, the
shaped catalyst structures were aged by continuing to
pass the n-butane-in-air stream over the catalyst for
5   approximately 24 hours. The thusly activated and
conditioned shaped catalyst structures were perfor-
mance tested as described in Example 5, below.

EXAMPLE 4

This example illustrates the preparation of an
10   iron/lithium-promoted vanadium phosphorus oxide
catalyst in accordance with the procedure described in
Example 1 of U. S. Patent No. 4,632,915.

A twelve-liter, round bottom flask equipped as
described in Example 1, above, except that it was
15   further equipped with a water-cooled Dean Stark trap
and a coarse-frit gas dispersion tube, was charged
with 8,300 mL of isobutyl alcohol. Stirring was
commenced and the isobutyl alcohol was cooled to a
temperature of from about 10° C to about 15° C. To
20   the cooled isobutyl alcohol was added a solution of
901.8 g (7.87 mol) of 85.5% H_3PO_4 and 343.4 g (2.42
mol) of P_2O_5 maintained at room temperature. The
resultant solution was cooled to a temperature of from
5° C to about 10° C. To this cooled solution was
25   added, with stirring, 963.0 g (5.29 mol) of V_2O_5, 1.35
g (0.032 mol) of LiCl, 0.96 g (0.017 mol or g-atom) of
iron powder, and an additional 1.0 L of isobutyl
alcohol. Anhydrous HCl (2037.0 g, 55.81 mol) gas was
added via the gas dispersion tube to the stirred
30   reaction mixture over a 4.67-hour period while
maintaining the temperature between 40° C and 50° C.
The solution was heated to reflux and maintained at
reflux for approximately two (2) hours. Thereafter,
5.4 L of distillate was removed at atmospheric
35   pressure over a period of five (5) hours, followed by
an additional 1.38-hour period of reflux, followed by
removal of an additional 1.5 L of distillate over a
2.36-hour period. The mixture was cooled and

quantitatively transferred to a porcelain dish and
dried in a box oven at 150° C for approximately 5.5
hours. The dried material was then transferred to
another box oven and heated in nitrogen at a

5 temperature between 250° C and 260° C for approxi-
mately three (3) hours, followed by gradual
replacement of the nitrogen atmosphere by air and
heating an additional three (3) hours to yield a grey-
black catalyst precursor powder.

10   The catalyst precursor powder was blended to
contain approximately four (4.0) weight % graphite and
compressed on a Stokes 512 Rotary Tableting machine
equipped with appropriate dies and punches to produce
the desired shaped catalyst structure, 1.27 cm

15 cylinders with a tablet density of approximately 1.90
g/cm^3. The 1.27 cm slugs were ground to produce a
tablet feed powder in the size range of from 18 mesh
(U.S. Standard Sieve Size, 1.00 mm) to 30 mesh (600
μm) and fed into the tableting machine equipped with

20 appropriate dies and punches to produce the shaped
catalyst structure of interest. The compaction
pressure was adjusted to produce structures with
average (side) crush strengths of from 13.3 N to 89 N
(3 lb to 20 lb). The characterizing properties of the

25 shaped catalyst structures produced are summarized in
Table 1. The thusly prepared shaped catalyst (precu-
rsor) structures were activated according to the
activation procedure described in U.S. Patent No.
4,632,915, except that the structures were charged to

30 a 2.10 cm inside diameter x 121.9 cm long (0.83 in.
inside diameter x 4 ft long) fixed bed tubular
reactor. Following the activation, the shaped
catalyst structures were conditioned by warming the
reactor at 1° C per hour to 400° C while passing a gas

35 stream containing 0.6 mol % n-butane in air over the
shaped catalyst structures, beginning at approximately
280° C. After the temperature had reached 400° C, the
shaped catalyst structures were aged by continuing to

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pass the n-butane-in-air stream over the catalyst for approximately 24 hours. The thusly activated and conditioned shaped catalyst structures were performance tested as described in Example 5, below.

TABLE 1

Ex. No.	Composition Empirical Form.	Type	Void Space, No.	Size, mm Height	Width	Side Crush Stren.[1], N	Vol.Rat.[2], %	Surface/ Vol.[3], cm[-1]	Bulk Dens.[4], g/cu
1A[5]	$VP_{1.15}Ox$	Cylinder	None	3.73	3.18	66.75	100.0	18.0	0.84
1B	"	"	Centered Core Hole[6,7]	4.76	4.76	35.60	89.0	17.0	0.87
1C	"	"	Grooves[8], 6	5.36	5.56	48.95	67.0	20.0	0.66
1D	"	"	Grooves[9], 3	3.97	3.97	35.60	61.0	27.0	0.64
1E	"	"	Grooves[10], 3	5.56	5.56	35.60	45.0	20.0	0.66
2A[5]	$VP_{1.2}Ox$	"	None	5.47	4.76	31.15	100.0	13.0	0.83
2B	"	"	Centered Core Hole[6,7]	4.76	4.76	35.60	89.0	17.0	0.96
2C	"	"	Grooves[9], 3	3.97	3.97	35.60	61.0	27.0	0.65
3A	$VZn_{0.01}Li_{0.002}P_{1.2}Ox$	"	Centered Core Hole[6,7]	4.29	4.76	31.15	89.0	17.0	1.09
3B	"	"	Grooves[9], 3	3.97	3.97	35.60	61.0	27.0	0.87
4A	$VFe_{0.0016}Li_{0.003}P_{1.2}Ox$	"	Centered Core Hole[6,7]	4.14	4.76	35.60	89.0	17.0	1.05
4B	"	"	Grooves[9], 3	3.97	3.97	31.15	61.0	27.0	0.87

[1]Average of at least 10 crush determinations.
[2](Geometric Volume of Shaped Structure/Geometric Volume of Solid Geometric Form) x 100.
[3]External Surface Area of Shaped Structures, cm^2/Geometric Volume of Shaped Structure, m^3.
[4]Determined by accurately weighing a given volume of settled shaped structures.
[5]Comparative example.
[6]1.58 mm diameter centered core hole.
[7]Centered centered core hole.
[8]See FIG. 4A and 4B.
[9]See FIG. 5A and 5B.
[9]See FIG. 1A and 1B.
[10]See FIG. 2A and 2B.

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EXAMPLE 5

Each·shaped catalyst structure type was
performance tested at a standardized set of reactor
conditions -- 1.5 mol % n-butane, 1.034 x 10^2 kPa-g
5   (15.0 psig) inlet pressure, and 2,000 GHSV. The
shaped catalyst structure of interest was charged to a
2.10 cm inside diameter x 121.9 cm long (0.827 in.
inside diameter x 4 ft long) reactor to its usable
height of 121.9 cm. In so doing, the amount of
10   catalyst charged to the reactor was a direct result of
the tube filling characteristics of the shaped
catalyst structure of interest. The catalyst was run
for at least 200 hours at the standardized performance
test conditions prior to carrying out yield
15   optimization. The maximum yield was determined for
each structure type by raising the n-butane conversion
until no further increase in reaction yield was
observed. The parameters and results are tabulated in
Table 2.

TABLE 2

Ex. No.	OST[1], hr	Catalyst Rx Char.[2], kg	Rx Char. Dens.[3], kg/m³ x10²	Temp, °C Bath	Temp, °C Hot Spot	Conv. mol %	Yield mol %	Yield wt %	Wt/Wt Prod. g MAN/kg cat-hr
1A	3,679	0.336	7.96	410	465	74.0	51.0	86.2	77.7
1B	1,657	0.303	7.18	439	490	79.0	50.0	84.5	84.5
1C	536	0.241	5.71	424	471	77.3	50.0	84.5	106.2
1D	1,500	0.253	5.99	421	474	80.0	53.0	89.6	107.3
1E	1,042	0.261	6.18	424	488	78.0	51.0	86.2	100.0
2A	647	0.311	7.37	408	449	76.3	49.9	84.3	82.2
2B	1,215	0.317	7.51	408	453	78.0	51.6	87.2	83.3
2C	815	0.276	6.54	405	455	78.1	53.0	89.6	98.3
3A	1,405	0.391	9.27	433	472	76.8	47.1	79.6	61.7
3B	794	0.335	7.94	433	486	76.0	49.0	82.8	74.9
4A	1,245	0.427	10.12	418	439	75.0	51.5	87.0	61.8
4B	1,210	0.339	8.033	428	454	75.0	52.0	87.9	78.5

[1]On Stream Time.
[2]Reactor Catalyst Charge.
[3]Reactor Charge Density.

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Comparison of the weight/weight productivity values obtained with the various shaped oxidation catalyst structures (compare Examples 1A with 1B, 1C, 1D, or 1E and 2A with 2B or 2C) clearly demonstrates
5 the advantages of the shaped oxidation catalyst structures of the instant invention over conventional catalyst shapes. In general, a similar comparison of weight % yield of maleic anhydride demonstrates equivalent or superior performance of the shaped
10 oxidation catalyst structures of the instant invention over the conventional prior art catalyst shapes. As a result, the combined advantage of equivalent or greater reaction yield using less catalyst (on a weight basis) provides a significant economic
15 advantage.

Thus, it is apparent that there has been provided, in accordance with the instant invention, shaped oxidation catalyst structures that fully satisfy the objects and advantages set forth
20 hereinabove. While the invention has been described with respect to various specific examples and embodiments thereof, it is understood that the invention is not limited thereto and many alternatives, modifications, and variations will be
25 apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications, and variations as fall within the spirit and broad scope of the invention.

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WHAT IS CLAIMED IS:

1. A shaped oxidation catalyst structure for the
production of maleic anhydride, which shaped structure
comprises a solid geometric form having at least one
(1) void space disposed in the external surface
thereof, the shaped structure being characterized by
(a) containing catalytic material comprised of mixed
oxides of vanadium and phosphorus, and (b) exhibiting
(i) a geometric volume of from about 30 percent to
about 90 percent of that exhibited by the void space-
free solid geometric form, (ii) an external geometric
surface area/geometric volume ratio of at least about
15 cm^{-1}, (iii) a bulk density of from about 0.4 g/cm^3
to about 1.4 g/cm^3, and (iv) a mechanical resistance
sufficient to maintain substantially the structural
integrity of the shaped structure under handling and
use conditions.

2. The shaped oxidation catalyst structure of
Claim 1 wherein the solid geometric form is selected
from the group consisting of cylinders, cubes, cones,
truncated cones, pyramids, truncated pyramids,
spheres, and prisms.

3. The shaped oxidation catalyst structure of
Claim 1 wherein the void spaces are equally spaced
over the external surface in which such void spaces
are located.

4. The shaped oxidation catalyst structure of
Claim 1 wherein the void spaces are selected from the
group consisting of grooves, holes, and dimples.

5. The shaped oxidation catalyst structure of
Claim 1 wherein the void spaces are selected from the
group consisting of angular and rounded shapes.

6. The shaped oxidation catalyst structure of
Claim 5 wherein the void spaces are rounded shapes.

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7. The shaped oxidation catalyst structure of Claim 1 wherein the geometric volume thereof is from about 40 percent to about 80 percent of that of the void space-free solid geometric form.

5   8. The shaped oxidation catalyst structure of Claim 1 wherein the external geometric surface area/geometric volume ratio is at least 20 cm^{-1}.

9. The shaped oxidation catalyst structure of Claim 1 wherein the bulk density thereof is from about

10   0.5 g/cm^3 to about 1.1 g/cm^3.

10. The shaped oxidation catalyst structure of Claim 1 wherein the mechanical resistance, as determined by side crush strength, is from about 4.45 N to about 222.4 N.

15   11. The shaped oxidation catalyst structure of Claim 10 wherein the side crush strength is from about 13.3 N to about 89 N.

12. The shaped oxidation catalyst structure of Claim 1 wherein the shaped structure exhibits a base

20   width of from about 3.175 mm to about 6.35 mm and a height/base width ratio of from about 0.5 to about 2.0.

13. The shaped oxidation catalyst structure of Claim 1 wherein the catalytic material is represented

25   by the empirical formula
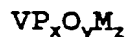
$$VP_xO_yM_z$$

wherein M is at least one promoter element selected from the group consisting of elements from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIB, and

30   VIIIB of the Periodic Table of the Elements, x is a number from about 0.5 to about 2.0, y is a number taken to satisfy the valences of V, P, and M in the oxidation states in which they exist in the composition, and z is a number from zero (0) to about

35   1.0.

14. The shaped oxidation catalyst structure of Claim 13 wherein x is a number from about 0.95 to about 1.35 and z is a number up to about 0.5.

15. The shaped oxidation catalyst structure of
5   Claim 13 wherein M is selected from the group consisting of elements from Groups IA and IIB of the Periodic Table of the Elements.

16. The shaped oxidation catalyst structure of Claim 15 wherein M from Group IA is lithium and from
10 Group IIB is zinc.

17. The shaped oxidation catalyst structure of Claim 13 wherein M is selected from the group consisting of elements from Groups IA and VIIIB of the Periodic Table of the Elements.

15   18. The shaped oxidation catalyst structure of Claim 17 wherein M from Group IA is lithium and from Group VIIIB is iron.
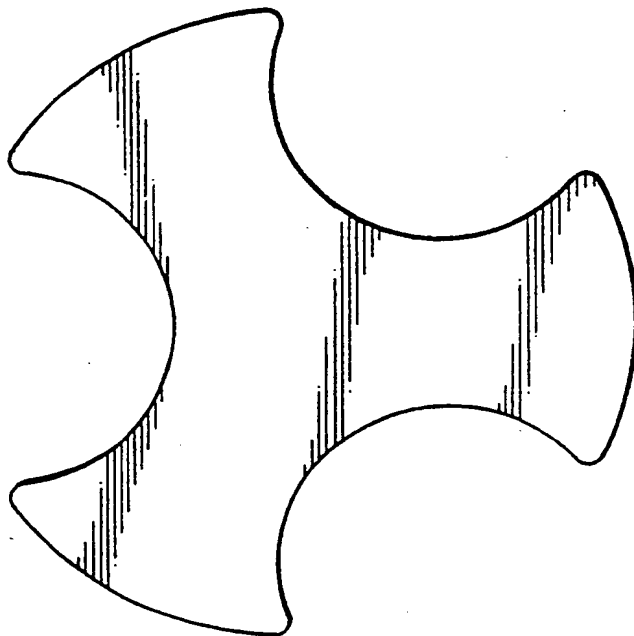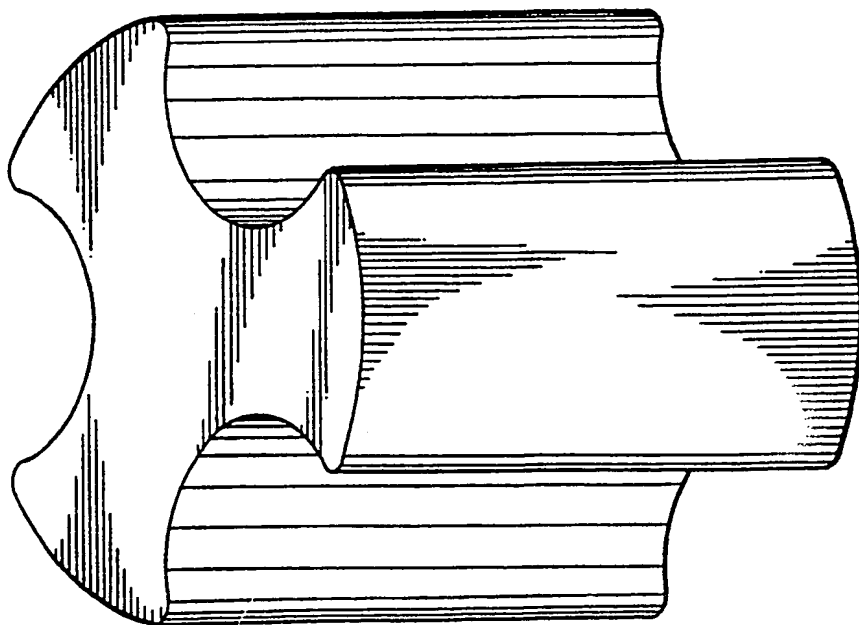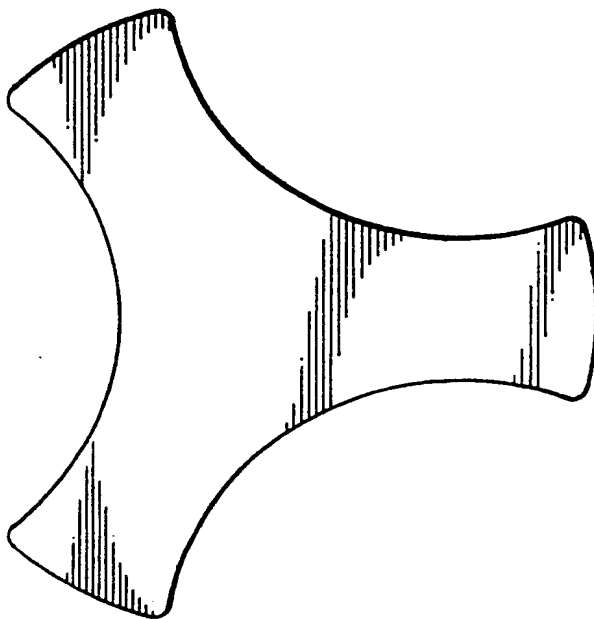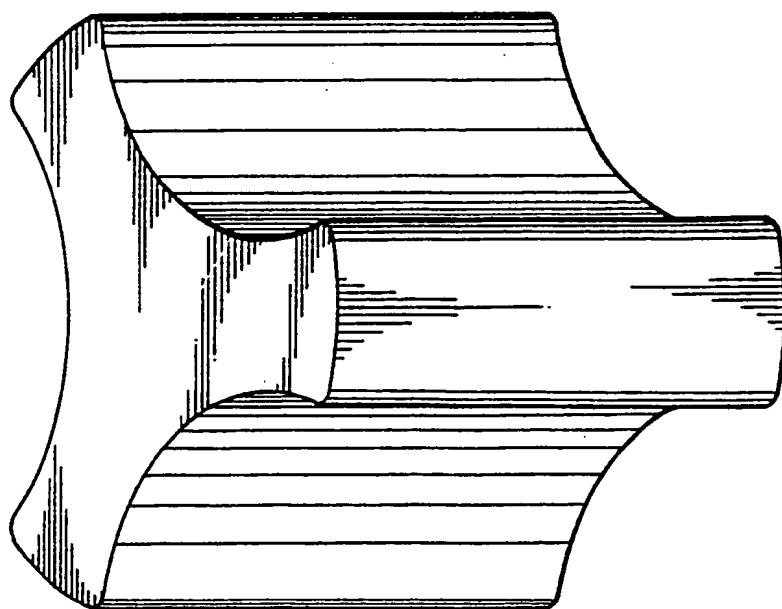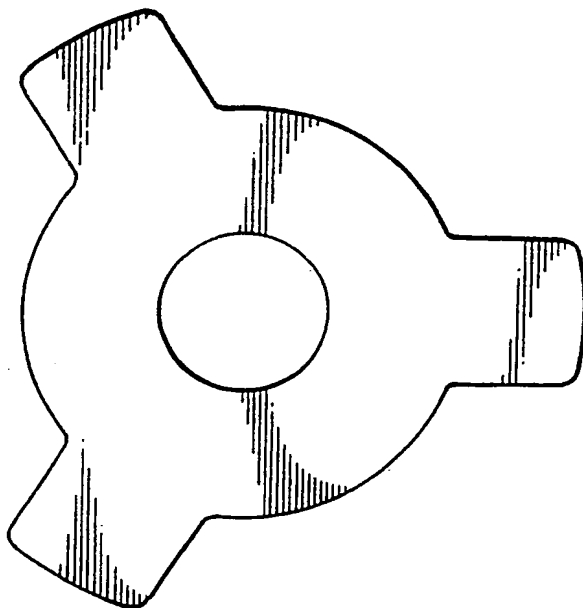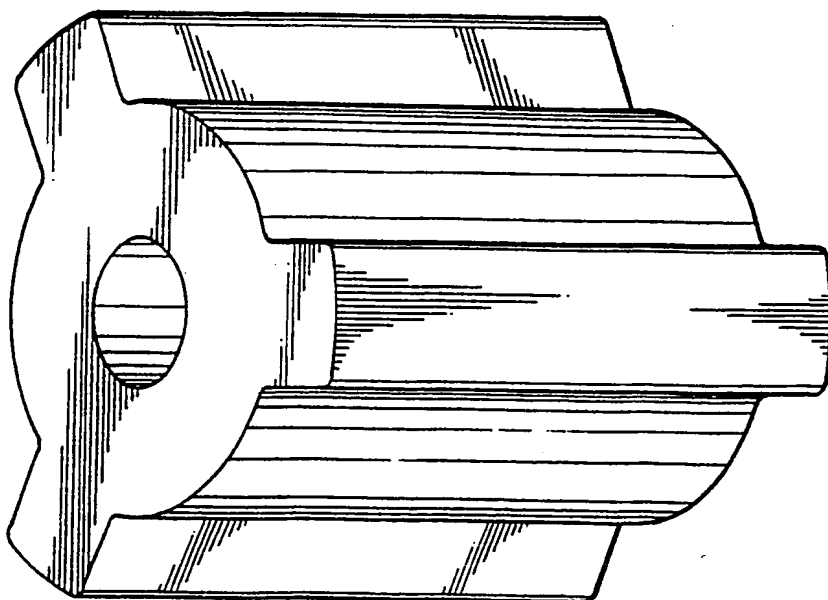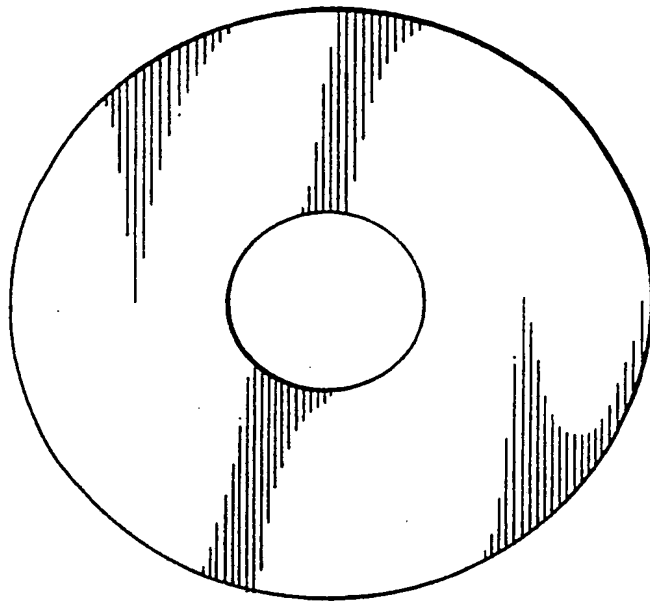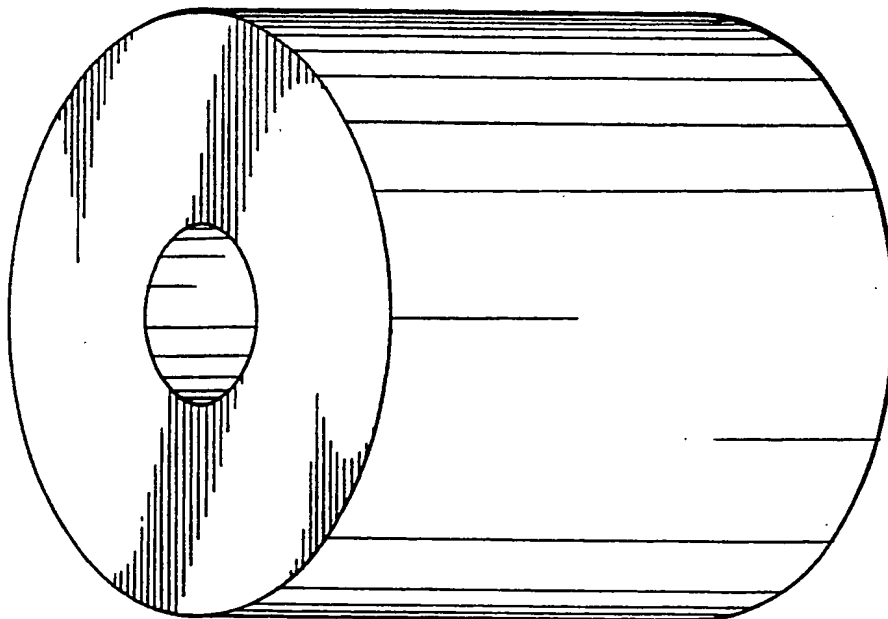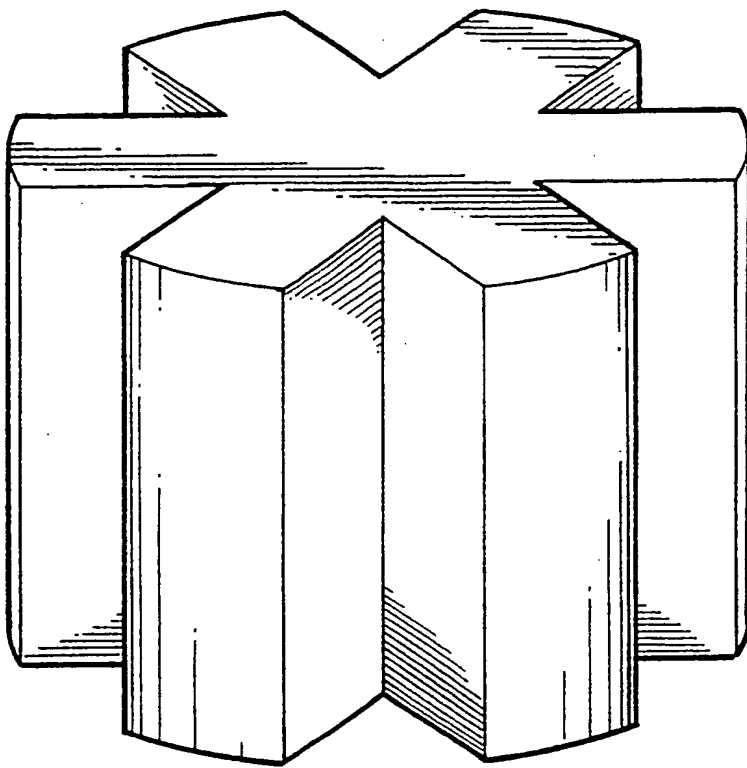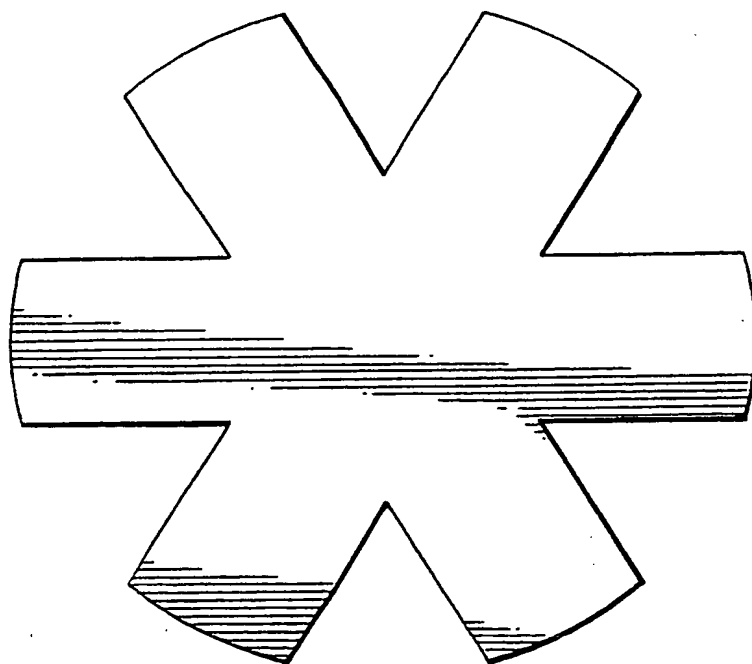
FIG. 1B

FIG. 1A

FIG. 2B

FIG. 2A

FIG. 3B

FIG. 3A

FIG. 4B

FIG. 4A

FIG. 5A

FIG. 5B
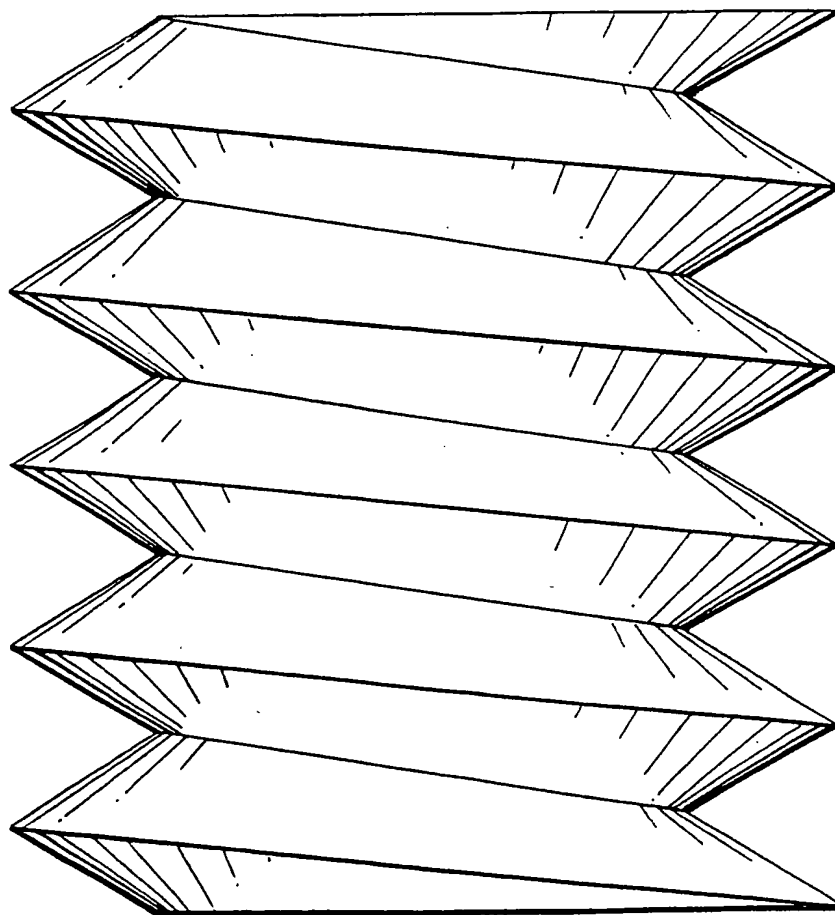
FIG. 6A
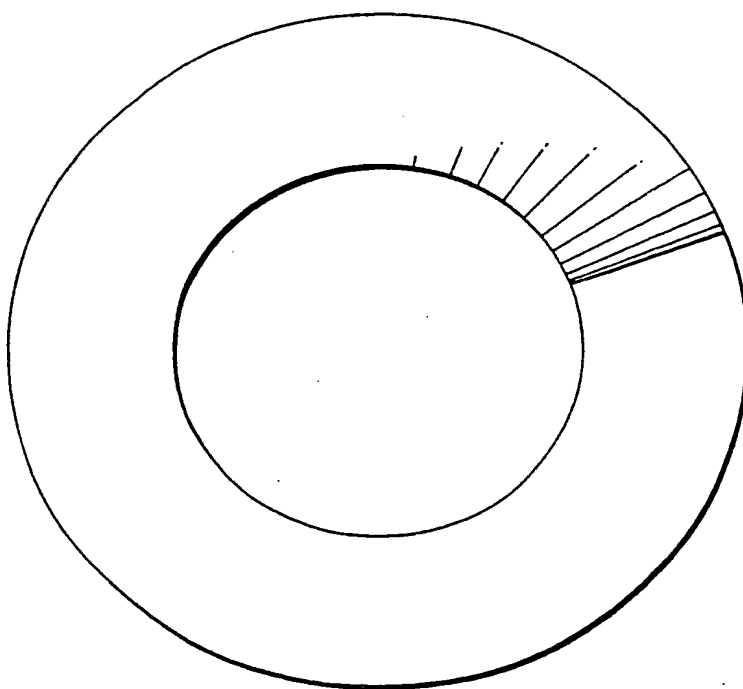
FIG. 6B
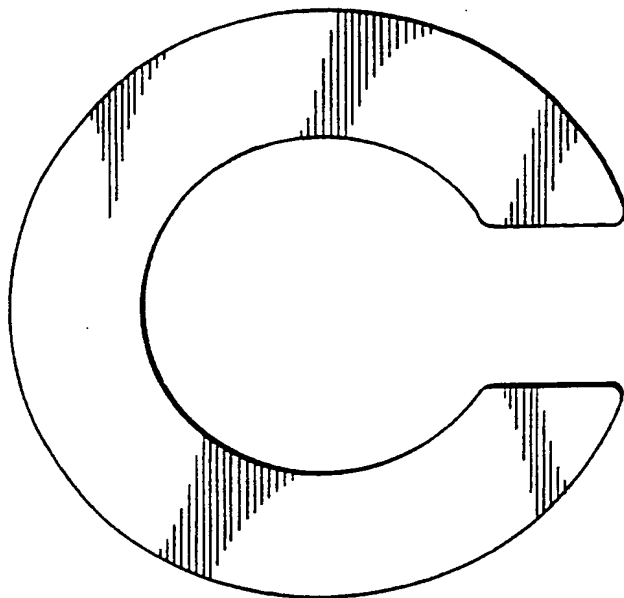
FIG. 7B
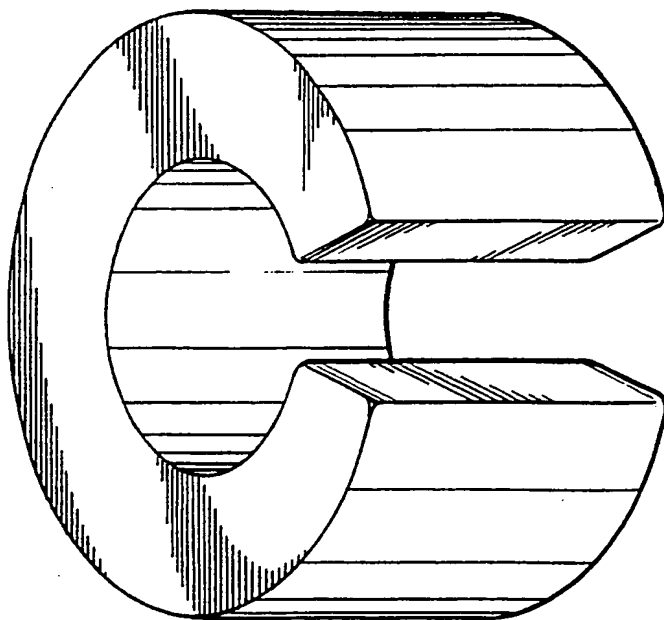
FIG. 7A
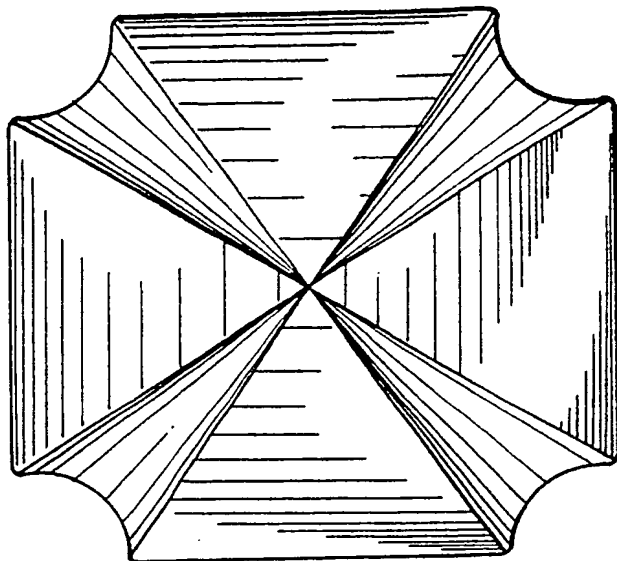
FIG. 8B
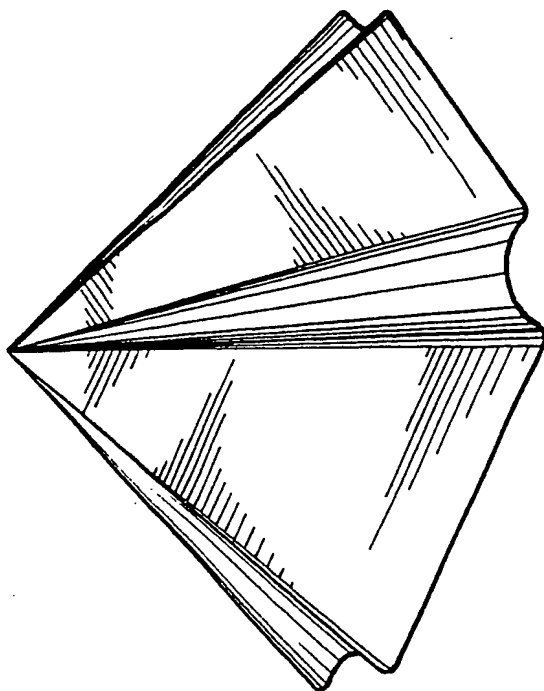
FIG. 8A
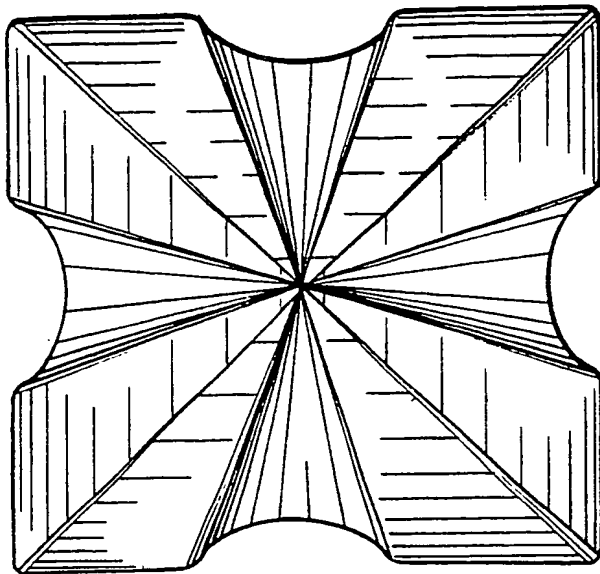
FIG. 9B
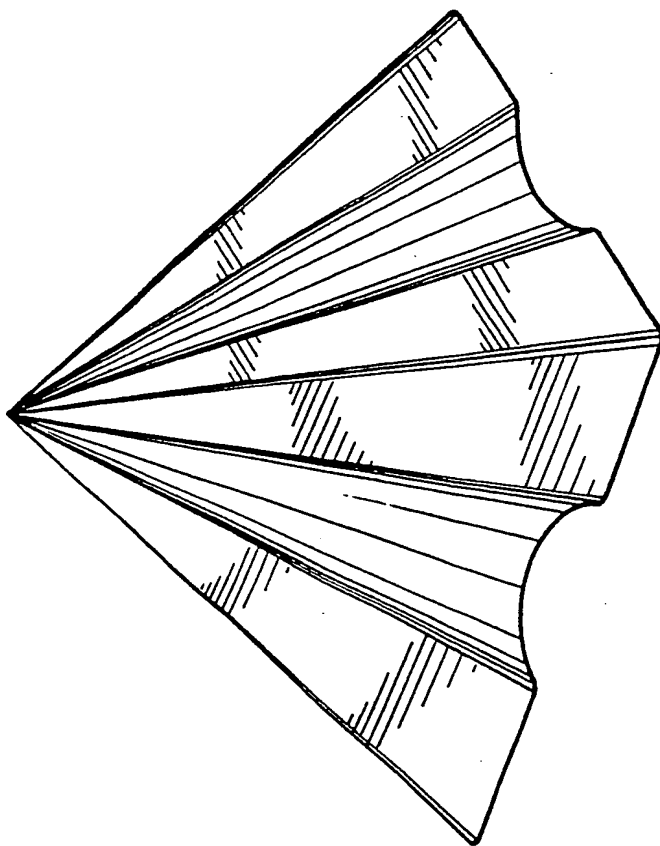
FIG. 9A
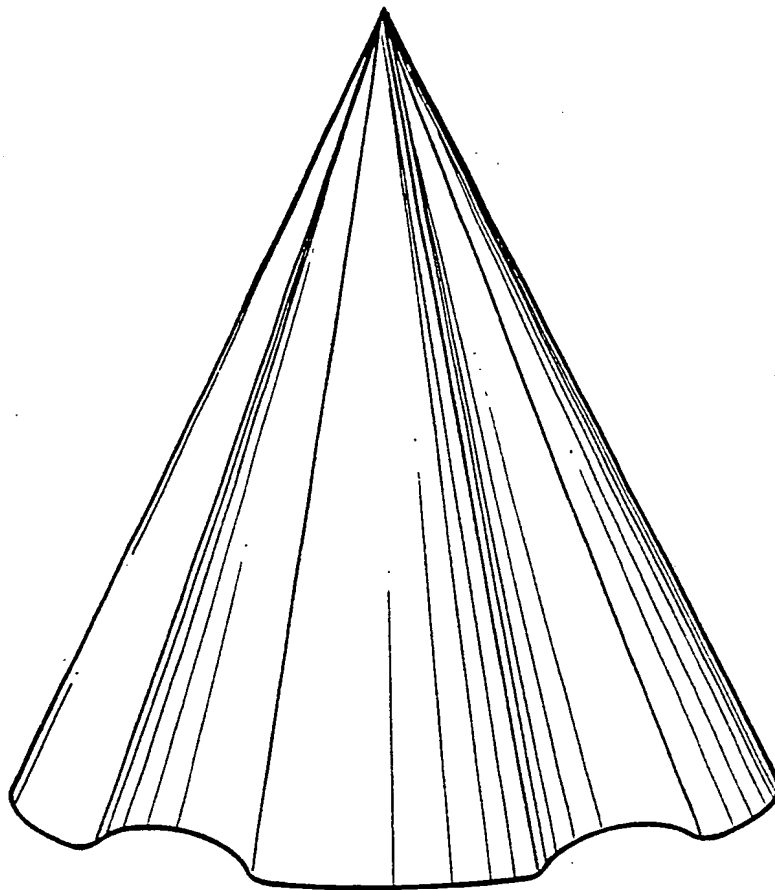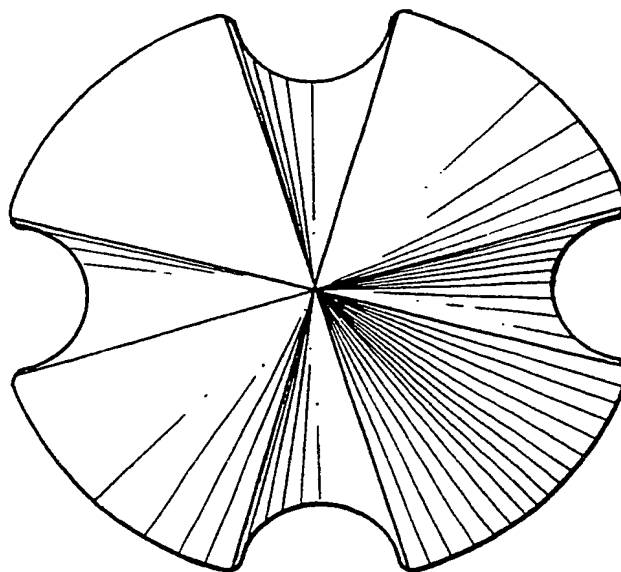
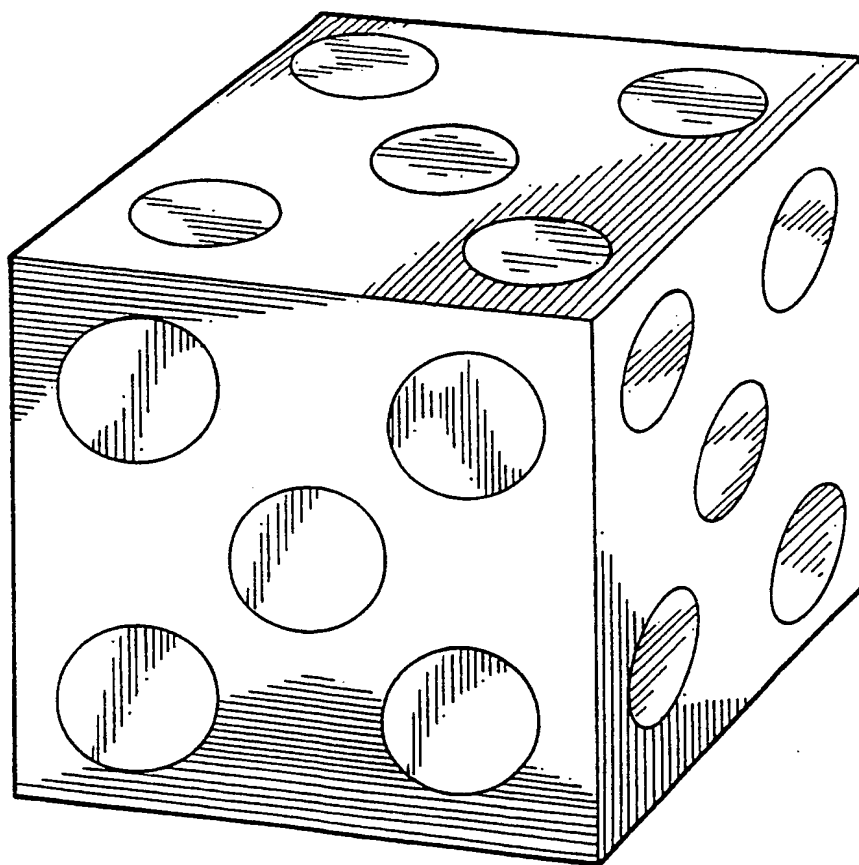FIG. 10A

FIG. 10B
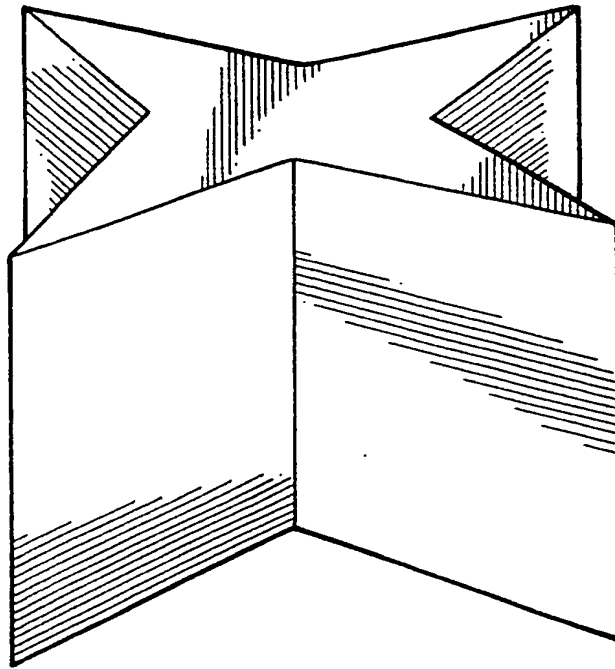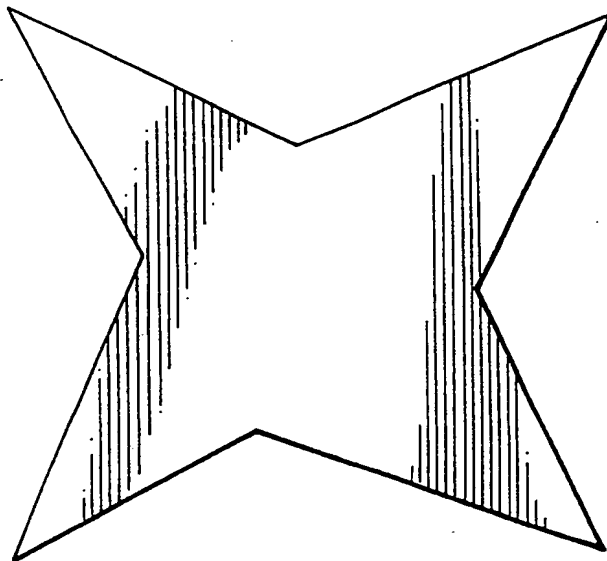
FIG.11A

FIG.11B
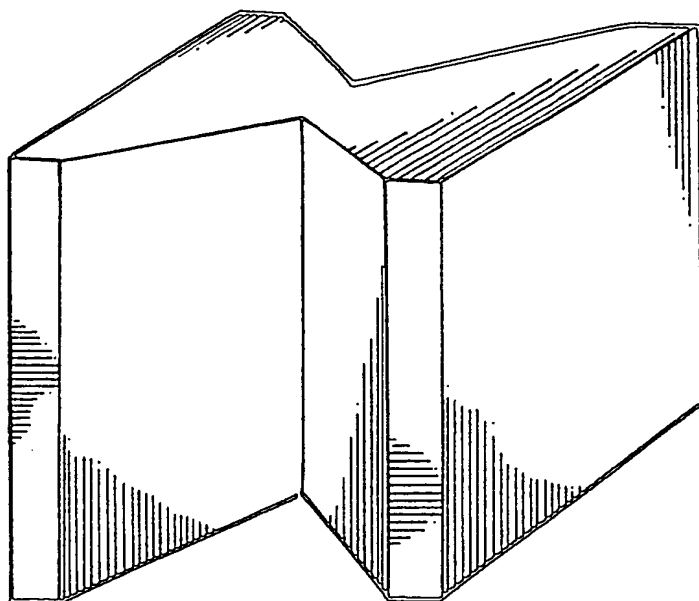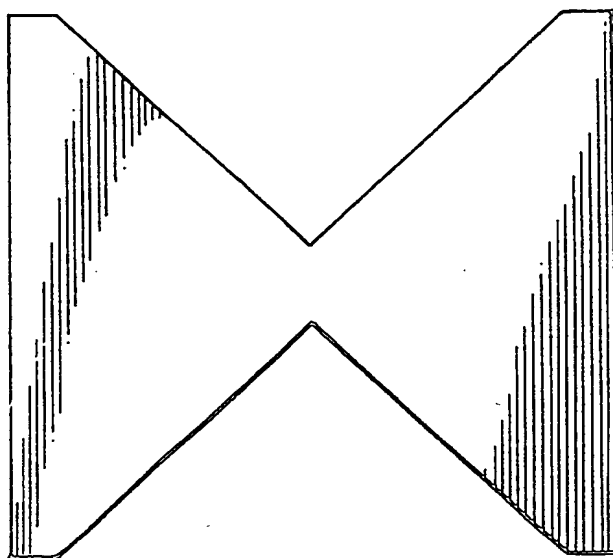
FIG. 12 A

FIG. 12 B

FIG. 13A

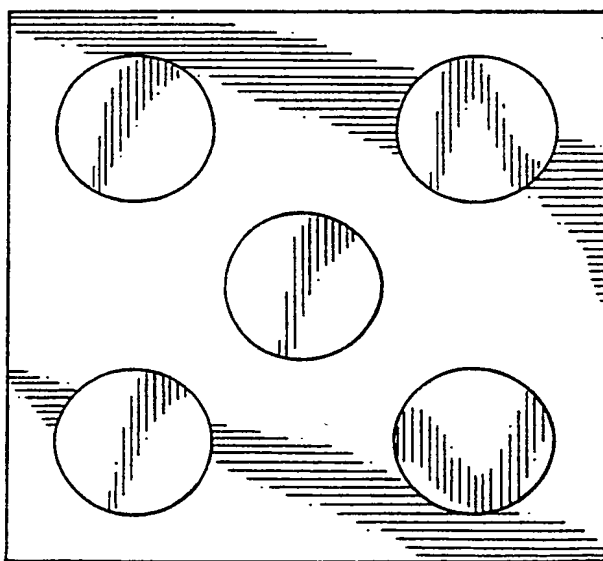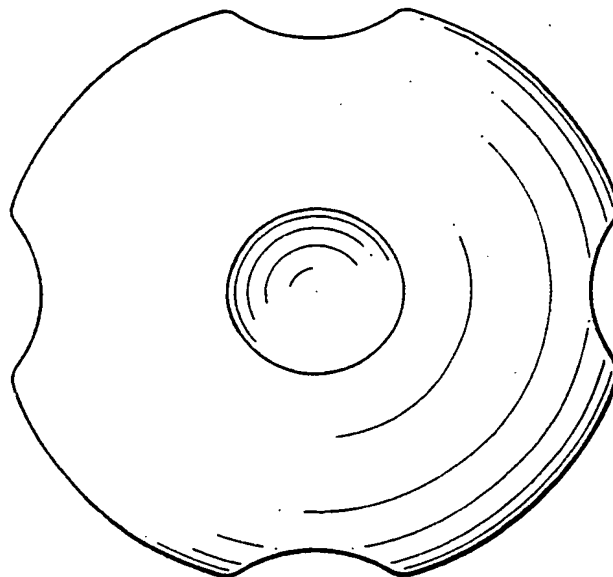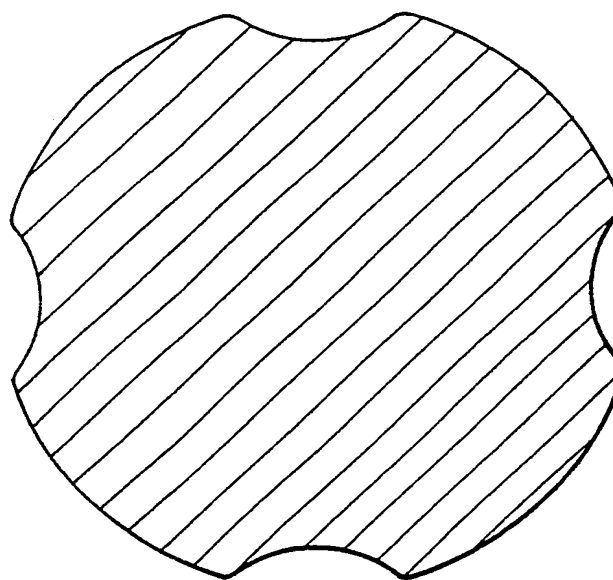FIG. 13B

FIG. 14A

FIG. 14B

INTERNATIONAL SEARCH REPORT

International Application No   PCT/US 91/07057

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶	
According to International Patent Classification (IPC) or to both National Classification and IPC	

Int.Cl. 5 B01J35/02;   B01J27/198;   C07C51/215;   B01J57/145

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.Cl. 5	B01J ; C07C

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category°	Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²	Relevant to Claim No.¹³
X	EP,A,0 184 790 (BASF) 18 June 1986 see page 8; claims 1-3 see page 4, line 6	1,2,4-8, 12
Y		3,9-11, 13-18

X	GB,A,1 373 351 (MONSANTO) 13 November 1974 see figure 11 see claims 1-10 see page 1, line 27 - line 33 see page 2, line 63 - line 65	1,2,4

Y	GB,A,2 193 907 (DYSON REFRACTOTIES) 24 February 1988 see page 1, line 112 - line 130	3

	-/--	

° Special categories of cited documents : ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
23 JANUARY 1992	- 6. 02. 92

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	THION M.A.

Form PCT/ISA/210 (second sheet) (January 1985)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	EP,A,0 107 274 (THE STANDARD OIL COMPANY) 2 May 1984 see claims 1,9,10 ---	9,13-15
Y	EP,A,0 221 876 (MONSANTO) 13 May 1987 see claims 1-4 ---	16-18
Y	EP,A,0 151 912 (MONSANTO) 21 August 1985 see page 33, line 14 - line 18 ---	10,11
A	EP,A,0 220 933 (MOBIL OIL) 6 May 1987 ---	
A	GB,A,2 046 118 (AMERICAN CYANAMID) 12 November 1980 ---	

III. DOCUMENTS CONSIDERED TO BE RELEVANT   (CONTINUED FROM THE SECOND SHEET)

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GB-A-2193907	24-02-88	None		
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EPO FORM P0459